ABSTRACT

Title of Thesis: MODELING OF THIN FILMS FOR SELF-CLEANING PURPOSES

Harika Vakkantula, Master of Science, 2017

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Surface self-cleaning efficiency depends on the rates of decontamination and contamination. It has been observed that the rate of decontamination increases when the surface is exposed to water, a process called as photoinduced superhydrophilicity. Understanding the reaction mechanism for photoinduced superhydrophilicity has been challenging over past decade. Several reaction mechanisms have been proposed but gaps in understanding these mechanisms elemental wise remain. Moreover, the reaction mechanisms proposed contradict the experiment results of the titanium dioxide interaction with water. Thus, it is essential to propose a reaction mechanism that is consistent with the experimental results. In the first part of the thesis, we fabricated titanium dioxide thin films by using the Atomic Layer deposition(ALD). Tetrakis-(dimethylamino) titanium (TDMAT) and ozone precursors are used to deposit photoactive titanium dioxide. Experiment results using these films are found to be promising. In the second part of the thesis we proposed potential elementary reaction mechanisms in supporting experimental evidence at each step of the reaction.

MODELING OF THIN FILMS FOR SELF-CLEANING PURPOSES

by

Harika Vakkantula

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List of Abbreviations

AFM	Atomic Force Microscopic
ALD	Atomic Layer Deposition
EPR	Electron Paramagnetic Resonance
HREELS	High Resolution Electron Energy loss Spectroscopy
UV	Ultra Violet

Chapter 1: Introduction

1.1 Motivation

The motivation to study self-cleaning surfaces is due to its high potential in reducing maintenance costs and environmental friendly cleaning. Self-cleaning surfaces are surfaces which are cleaned with the help of natural phenomena [4]. Self-cleaning surfaces have a wide range of applications in indoor and outdoor applications such as windows, roof tiles and solar panels. Over time, windows are covered by dust and in order to remove the dust we use water and soap, which requires mechanical work. Self-cleaning surfaces require minimal amount of water and no mechanical work for the surface cleaning.

Photocatalytic organic degradation is a well-known phenomena in which the organic dirt breaks down into less harmful products such as carbon dioxide and water. In the early 1990's researchers found that in the presence of sunlight and water, the surface became superhydrophilic and water carried away the dirt particles [24]. This phenomenon is called photo-induced superhydrophilicity and this mechanism occurs in parallel with photocatalytic organic degradation.

The reaction mechanism for the photoinduced hydrophilic surface is not understood clearly. Based on experimental studies, various hypothesis were proposed

to explain the photoinduced hydrophilicity reaction mechanism. The main idea of this thesis is to study the surface interactions of titanium dioxide with water, propose potential elementary reaction mechanisms of photoinduced hydrophilicity and to develop self-cleaning thin films using Atomic Layer Deposition(ALD).

1.2 Self-cleaning surfaces

As discussed in the previous section, self-cleaning surfaces are surfaces which get cleaned easily with the help of natural phenomena such as rain. Self-cleaning surfaces are broadly divided into two categories: hydrophilic and hydrophobic surfaces. The property of these surfaces depends upon the affinity of water towards the surface [25]. For a hydrophilic surface, when water droplet falls on the surface the water droplet spreads. The dirt particles are adsorbed by water and are carried away by water. For hydrophobic surfaces, the water droplet rolls off and carries dirt particles with it. The rate of removing dust particles is faster with hydrophobic surfaces because hydrophobic surfaces are water repellent, and thus possess low adhesive force with water, which makes the dust particles to roll off the water from the surface quickly. However, for a hydrophilic surface due to its strong affinity towards water the removal of dirt particles is slower [4].

1.3 Surface property of a self-cleaning material

The hydrophilic and hydrophobic property of the surface is determined by the contact angle of the solid surface with water. The contact angle is defined as the

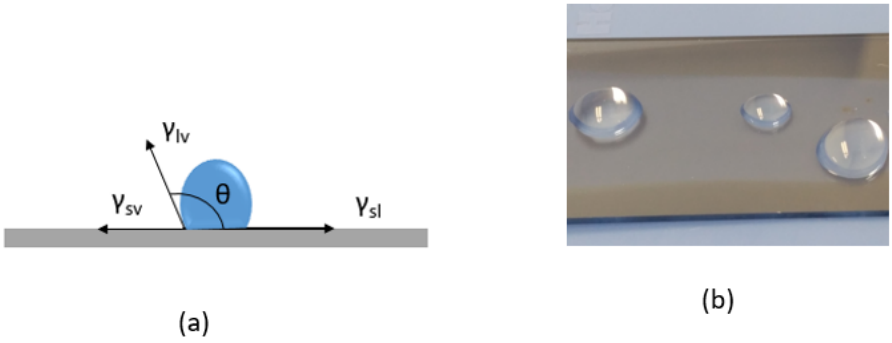


Figure 1.1: (a) Schematic figure of contact angle with a solid surface, (b) Contact angle of water on the titanium dioxide thin film fabricated by ALD before UV illumination.

angle between the solid-liquid interface and liquid-vapor interface as shown in the figure (1.1 (a)). The contact angle before UV illumination is called as initial contact angle.It has been observed that the initial contact angle of the surface depends on the surface roughness [19]. The relationship between contact angle and wettability of the surfaces are as shown in Table (1.1). For a super hydrophilic surface the contact angle is less than 5^o. At equilibrium conditions, the surface property of the solid surface is determined by using Young's equation(1.1).

$$\gamma_{sv} + \gamma_{lv} = \gamma_{sl} cos\theta \tag{1.1}$$

where θ is the contact angle , γ_{sv} is the surface free energy per unit area of solid and vapor interface, γ_{lv} is the free energy per unit area of liquid and vapor interface

Table 1.1: Contact angle of different wettable surfaces.

Contact angle	surface property
$\theta < 5^o$	Super Hydrophilic
$\theta > 5^o$ $\theta < 90^o$	Hydrophilic
$\theta > 90^o$	Hydrophobic
$\theta > 150^o$	Super Hydrophobic

and γ_{sl} is the free energy per unit area of liquid and solid interface.

The equation developed by Young et al is valid for ideal surfaces with no roughness [6]. For the uneven surfaces, Wenzel modified Young equation by considering surface roughness in equation(1.2) [4].

$$\cos\theta' = r\cos\theta \tag{1.2}$$

where θ' is the apparent contact angle, θ is the actual contact angle and r is the surface roughness factor. The surface roughness factor is defined as the ratio of the geometrical surface area and the actual area. For rough surfaces based upon the value of r the effect of hydrophilic changes. For $r > 1$, as r increases hydrophilicity increases.

1.4 Photocatalysis

The increase in the rate of a chemical reaction in the presence of catalyst when exposed to sunlight is called photocatalysis. The photocatalysts in self-cleaning surfaces are the semiconducting materials deposited on the top of the glass or solar panels. The self-cleaning process is a heterogeneous photocatalysis process in which

solid-phase and liquid-phase reactions are involved; the solid phase is the semiconductor thin film and liquid phase is water. When the semiconducting thin film is exposed to sunlight, the photons with energy greater than the band gap energy of photocatalyst are absorbed by the photocatalyst and electrons from valence band jump to conduction band producing electrons and holes in the lattice [6]. These electrons and holes participates in surface redox reaction, which decompose the dirt and increases the hydrophilicity of the surface.

Two simultaneous reactions happen on the self-cleaning surface, photocatalytic organic degradation and photoinduced superhydrophilicity. In photocatalytic organic degradation reactions, the photogenerated electrons and holes react with water vapor and molecular oxygen producing superoxide and hydroxyl radicals. The radicals produced by surface reactions are highly active species which further decompose organic matter and produces less harmful products such as water and carbon dioxide. In photoinduced hydrophilic reaction the photo generated electrons and holes get trapped in lattice sites and react with adsorbed water on the surface which modifies the surface structure of the semiconducting materials. The change in the surface structure increases the affinity of water with the surface, which results in the formation of hydrophilic surface.

1.5 Outline of thesis

The thesis is organized as follows. Chapter 1 explains the background information of self-cleaning surface. Chapter 2 gives the background on the several proposed

reaction mechanisms and their drawbacks and overview of Atomic Layer Deposition (ALD) methods used to deposit photoactive titanium dioxide thin film. In this chapter we also discuss about the experimental support to the potential elementary reactions that take place in photoinduced hydrophilic process. Chapter 3 discusses about the experiments performed to deposit titanium dioxide using TDMAT and ozone precursors. In chapter 4, the potential elementary reaction mechanisms for photoinduced hydrophilic process are discussed.

Chapter 2: Background and literature review

2.1 Photo induced hydrophilic surface

The changes in surface properties of thin semiconducting films when exposed to sunlight and water was discovered accidentally in TOTO LTD laboratory [24]. In this study the initial water contact angle of the film surface is 72^o but when the surface is exposed to sunlight and water the contact angle changes to 0^o [24]. The surface property changed from hydrophobic to hydrophilic in the presence of sunlight and this superhydrophilic film when placed in dark conditions returned to being a hydrophobic film as shown in the figure(2.1). This change in surface property is called photoinduced superhydrophilicity.

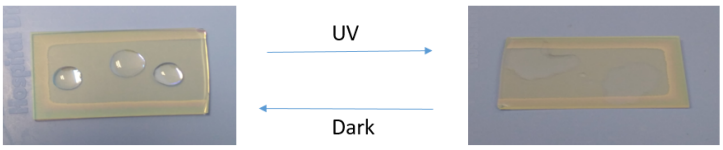


Figure 2.1: The change in the wettability of the fabricated titanium dioxide thin film when placed under UV illumination and in dark conditions.

2.2 Titanium dioxide

Semiconducting materials such as titanium dioxide and zinc oxide are widely used as self-cleaning surfaces. Titanium dioxide is the most studied material because of its varied range of applications such as a photocatalyst, self-cleaning surfaces, water purification, and anti-fogging [4]. Titanium dioxide can be found in three main forms of the crystal structure rutile, anatase, and brookite. Experimental studies of self-cleaning materials are mainly done with anatase and rutile titanium dioxide. The brookite crystal structure of titanium dioxide is not abundant and very difficult to prepare [6].The rutile structure with crystal face (110) is thermodynamically stable. The band gap energy for anatase crystal structure is 3.2 eV and for rutile is 3.0 eV. The maximum wavelength of light that can be absorbed by the semiconducting material is 380 nm, which is restricted to the UV irradiation range. Titanium dioxide based catalysts are widely used photocatalysts due to their high stability, low cost and environmentally friendly nature.

It has been observed that titanium dioxide surface when exposed to sunlight, the surface becomes amphiphilic. The surface which has both hydrophilic and oleophilic properties is called as amphiphilic surface. For an oleophilic surface, when oil drop falls on the surface the oil spreads. The Atomic Force Microscopic (AFM) studies of the photoexcited surface demonstrated the presence of hydrophilic and oleophilic domains on titanium dioxide [25]. The photoinduced amphiphilicity is a unique property of titanium dioxide, which is not exhibited by any other semiconducting material [24]. This unique property made titanium dioxide more favorable

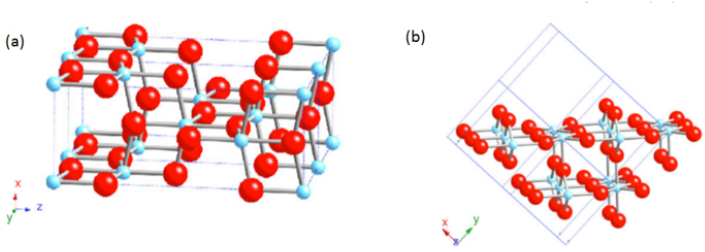


Figure 2.2: The crystalline structure of titanium dioxide (a) anatase (001), (b) rutile (110) (taken from Fujishima et al [6]).

material for self-cleaning. The bulk phase of titanium dioxide has six coordinated titanium atoms and three coordinated oxygen atoms whereas the surface of titanium dioxide consists of five coordinated titanium atoms and two coordinated oxygen as shown in the figure(2.2). The change in the surface structure and bulk structure of the titanium dioxide is one of the driving forces for the photoinduced hydrophilic reaction.

2.3 Deposition methods for titanium dioxide thin films

Titanium dioxide thin films are deposited by liquid or gas phase deposition methods. The liquid-phase deposition methods generally produces amorphous films and in order to get a crystalline film, a post annealing process is required. Sol gel deposition is the most widely used liquid-phase deposition method to prepare photocatalytic titanium dioxide films, but the temperature required for annealing is very high [16]. To produce thin films on heat sensitive materials such as polymers and fibers the amorphous thin film is processed through hydrothermal treatment to

obtain crystalline film [11].

Gas phase deposition methods capable of producing crystalline films include Chemical Vapour Deposition (CVD) and Atomic Layer Deposition (ALD). The film quality for vapor phase methods can be high in comparison with liquid phase methods and vapor phase methods may not require any post processing steps to obtain crystalline film.

2.4 Atomic layer deposition

Atomic layer deposition is a gas phase thin film deposition technique which is used to grow thin films with precise thickness by controlling growth at the atomic level [18]. In this method, the precursors in vapor form are pulsed alternatively into the reactor one after the other. Purge gas is fed to the reactor in between the precursor pulses to remove the unreacted precursors and byproducts. During the first half cycle, the precursor is adsorbed on the surface of the substrate and partially decomposes. When the second precursor is pulsed into the reactor, additional surface reactions take place completing the reaction cycle. This results in the formation of desired sub mono-layer thin film. As the number of cycles increases the thickness of the thin film increases.

Atomic layer deposition is unique in that it has self limiting growth mechanism. This mechanism gives high quality thin films with control over film thickness [10]. This characteristic of the Atomic layer deposition is driving factor to consider it as viable process to deposit different types of titanium dioxide films that exhibits photo

induced hydrophilic property. The precursors used in the deposition of titanium dioxide are of titanium source and oxygen source.

2.5 Background on Atomic layer deposition of titanium dioxide

This section gives an overview of different precursors used in ALD of self-cleaning material. The titanium precursors include halides, oxides such as Titanium fluoride, Titanium methoxide and Tetrakis-(dimethylamino) titanium (TDMAT). The oxygen sources used for titanium dioxide deposition includes water, hydrogen peroxide and ozone.

2.5.1 ALD process using titanium halides precursor

Titanium dioxide thin films can be deposited by using TiF_4 as titanium precursor and water as oxygen precursor. Pore et al studied the deposition of titanium dioxide thin film by ALD method at substrate temperature 300^oC-500^oC [18]. Film properties and variations of the growth at 300^oC, 400^oC and 500^oC of the deposited film. Two different substrates, borosilicate and soda lime were used in this experimental study. The growth rate was in the range of 0.8 Å-1.1 Å/cycle and the thickness of the deposited photocatalytic films is in the range of 100 nm - 150 nm. The results from this analysis revealed that a change in substrate changed the growth rate. The film characteristics were determined by using X-ray diffraction and from these studies all the films deposited were shown to have crystalline structures. The studies on photoinduced hydrophilicity revealed that the films deposited at high

temperature under UV illumination converts to hydrophilic film very quickly [18].

2.5.2 ALD process using titanium alkoxide precursors

Photocatalytic titanium dioxide thin film is deposited in this process by using titanium methoxide $Ti(OCH_3)$ and water. Pore et al studied the film characteristics and photocatalytic properties for the films deposited in the range of at temperature 200^oC-400^oC. The films were deposited on glass substrates and the deposited thickness of the film is in the range of 60 nm -150 nm at different temperatures. X-ray diffraction was used to study the film characteristics which determined that the films deposited at 200^oC are amorphous and the films deposited at 400^oC are crystalline [17]. Photocatalytic activity of these films were studied by analysing the decomposition of methylene blue when exposed to UV light. The results from these studies showed that the films deposited at 200^oC did not show photocatalytic property because they are amorphous and the films deposited at all other temperatures above 200^oC demonstrated photocatalytic properties [17].

2.5.3 ALD process using titanium alkylamide precursors

Titanium dioxide is deposited in this process using tetrakis - (dimethylamino) titanium (TDMAT) as the titanium precursor and water or ozone as oxygen precursor. TDMAT has higher reactivity with water precursor relative to titanium halides because of high bond energy of titanium halide [1]. A crystalline titanium dioxide film was obtained for temperatures above 200^oC and amorphous titanium dioxide

films was obtained around 165^oC [10]. The growth rate of the films deposited by using TDMAT as precursor is approximately 0.55 Å/cycle and the thickness of the deposited films was approximately of 100 nm. The studies on this deposition process revealed that for the water precursor, as the temperature increases growth rate decreases and for the ozone precursor the growth rate increases. The reason for this growth behaviour was attributed to evaporation of reactive species, hydroxyl groups for the water precursor [10].

2.6 Background on elementary reactions in photoinduced superhydrophilicity

2.6.1 Generation of electron-hole pair

Holes and electrons are produced by the absorption of the photons from the sunlight source. When the photon energy is greater than the band gap energy, an electron from the valence band jumps to conduction band, leaving holes behind in the valence band [27]. These electrons and holes take part in surface redox reactions for photo induced hydrophilicity and photocatalytic organic degradation. The band gap of titanium dioxide is 3.2 eV for anatase phase and 3.0 eV for rutile phase, and because of the high band gap it can absorb only UV illumination. The efficiency of the photoinduced process is limited by recombination of electrons and holes. According to the time scales of charge recombination process and molecular oxygen reduction reaction, they are competitive reactions [6]. In order to inhibit recombination reactions charge carrier trapping is required. Charge carrier trap-

ping also increases the quantum yield of the process [27]. Quantum yield (QY) is approximately the ratio of rate of the charge transfer to the rate of total charge generation.

$$QY \approx \frac{k_t}{k_t + k_r} \tag{2.1}$$

where k_t is the rate of charge transfer and k_r is the rate of recombination (surface and bulk).

2.6.2 Charge separation, transfer and surface reactions

As discussed in the earlier section the photoexcited electrons and holes recombine and produce heat energy. The recombination of electrons and holes decreases the number of holes and electrons which reaches the surface. This will adversely affect the formation of hydrophilic domains or the surface redox reactions. There are two types of recombination: surface recombination and bulk recombination, both of which inhibit the electron and hole transfer to the surface sites and their surface reactions. Trapping of electrons and holes inhibits recombination and increases diffusion of electrons and holes to the surface [9]. Photoexcited charges are trapped in deep traps and shallow trap sites. The shallow and deep trap sites are formed in crystal lattices due to the imperfections in the crystal lattice. Generation of holes and electrons and bulk and surface reactions in titanium dioxide film is shown are figure(2.3).

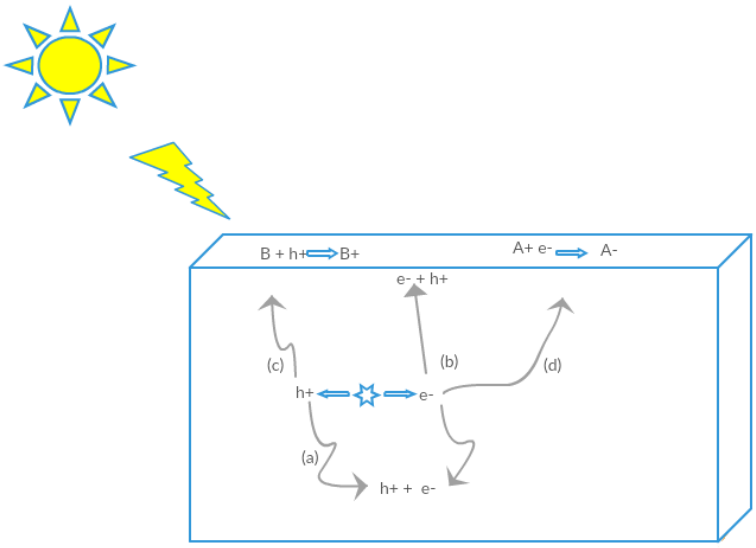


Figure 2.3: Schematic figure representing several reactions in titanium dioxide a) bulk recombination, b) surface recombination c) surface oxidation reaction d) surface reduction reactions.

Trapped electrons and holes are detected by using Electron Paramagnetic Resonance (EPR) technique. Studies using EPR and Infrared spectroscopy(IR) conducted by Berger et al [21] demonstrated that the majority photo generated electrons exists as free electrons and in the form of Ti^{+3} signal. Raftery et al [2] conducted NMR studies which demonstrated that the reaction of shallow trapped holes with chemisorbed species is very fast, whereas deep trapped holes react rapidly with physisorbed species.

2.6.3 Dissociative or molecular adsorption of water

Surface interactions of the titanium dioxide surface with water has been extensively studied due to its wide applications in photocatalysis and the photoinduced

hydrophilic effect. Experimental studies were done on stoichiometric and reduced surfaces of titanium dioxide surfaces. The reduced surface contains oxygen vacancies whereas the stoichiometric surface does not contain any vacancies. Henderson et al [8] observed that the molecular adsorption happens on the stoichiometric surface and dissociative adsorption of water happens on reduced surfaces by using High Resolution Electron Energy loss Spectroscopy (HREELS).

2.6.4 Formation of hydroxyl ions on the surface

The photo-generated holes and electrons which reach the surface of the titanium dioxide film participate in redox reactions. As discussed in the earlier section, the trapped holes at oxygen lattice sites create oxygen vacancies or make the bond between titanium and oxygen weaker. In the mechanism developed by Wang et al [25], when water is adsorbed on the reduced titanium dioxide surface, dissociative adsorption of water occurs and results in the formation of hydroxyl groups releasing protons. Whereas, the mechanism explained by Sakai et al [19] demonstrated that the adsorption of water on the surface at titanium sites with a weaker bond between titanium and oxygen results in breakage of the bond between titanium and oxygen and thus forming hydroxyl groups on the surface of the titanium dioxide releasing protons.

The hydroxyl groups formed by this process are defined to be in metastable stage [28]. This stage is defined as the metastable state because of the reverse process, hydrophilic to hydrophobic conversion in dark conditions. This happens due

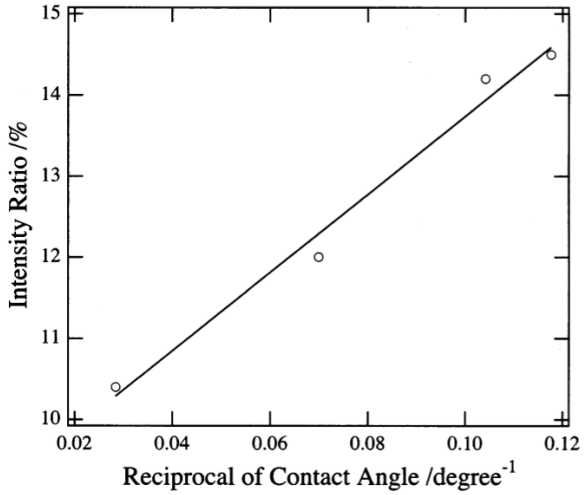


Figure 2.4: The plot showing the relationship between intensity ratio of surface hydroxyl groups and contact angle (taken from Sakai et al [19]).

to the low desorption energy of the hydroxyl groups and absence of photogenerated electrons and holes. The formation of hydroxyl groups on the surface results in the superhydrophilic film. The relationship between number of hydroxyl groups and contact angle is shown in figure(2.4). The X-ray Photoelectron Spectroscopy (XPS) analysis of O 1s band suggests that as the density of hydroxyl groups increases as the contact angle decreases [19].The intensity ratio is defined as the ratio of surface hydroxyl groups and O 1s band (oxygen lattice site).

2.6.5 Desorption of hydroxyl groups from the surface

In dark conditions, the film property changes from hydrophilic state to hydrophobic state. This change in film property is due to the desorption of hydroxyl groups from the surface, which reverts the reconstructed hydroxyl group to the

original titanium dioxide film. The studies on the reverse process revealed that the hydroxyl groups desorbs in the form of H_2O and O_2 or H_2O_2. Temperature programmed desorption studies on the interaction of water with the titanium dioxide films determined that the desorption energy of hydroxyl group is low, which leads to desorption of hydroxyl groups from the surface [19].

The experimental studies on the change in contact angle in dark conditions demonstrated that the rate of the dehydroxylation process is slower than the photo-induced hydrophilic process [19].

2.6.6 Adsorption of molecular oxygen

Molecular oxygen plays a vital role in charge separation and photocatalysis reaction. As discussed in the earlier section, the photogenerated electrons are detected in the form of Ti^{+3} ions. These photogenerated electrons are captured by the molecular oxygen adsorbed at the titanium sites forming superoxide ions [6]. These superoxide ions then participates in surface reactions with organic dirt to produce less harmful products.

$$Ti^{+4} + e^{-} \longrightarrow Ti^{+3}$$

$$Ti^{+3} + O_2(ads) \longrightarrow Ti^{+4} + O_2^{-}(ads)$$

The experiments performed by Berger et al [21] revealed that the concentration of trapped holes and super oxide ions are same. The results of this study demonstrated that the capture of photogenerated electrons by molecular oxygen not only inhibits recombination but also improves charge separation. The active oxygen

species such as superoxide ions and hydrogen peroxide,both of which participate in reduction reactions of photocatalytic organic degradation are generated in this reaction step. Hydrogen peroxide is formed by reaction with two superoxide ions and protons. The spectroscopy studies done by Atwood et al [3]and Goto et al [7] support the formation of hydrogen peroxide on the rutile and anatase titanium dioxide surface respectively. The molecular oxygen also regulates the surface irregularities which results in maintaining the stoichiometry of the titanium dioxide.

2.6.7 Fate of the proton

Formation of hydroxyl groups results in the release of protons to maintain the charge balance. The proton reacts with superoxide anion to form a radical $HO_2^{\cdot}$ [6], which further participates in photocatalytic organic degradation reactions. Reaction between protons and super-oxide anion also forms hydrogen peroxide. Hydrogen peroxide is one of the active oxygen species which takes part in photocatalytic organic degradation.

$$H^+ + O_2^{\cdot -} \longrightarrow HO_2^{\cdot}$$

$$2H^+ + 2O_2^{\cdot -} \longrightarrow H_2O_2 + O_2$$

Scanning Tunneling Microscope (STM) studies done by the Wendt et al [26] demonstrated that the protons released from the water molecule jump to the nearby bridge hydroxyl groups. The water molecules adsorbed on the titanium sites act as tunnel for protons to form bridge hydroxyl groups at neighbouring oxygen sites as shown in the figure (2.5).

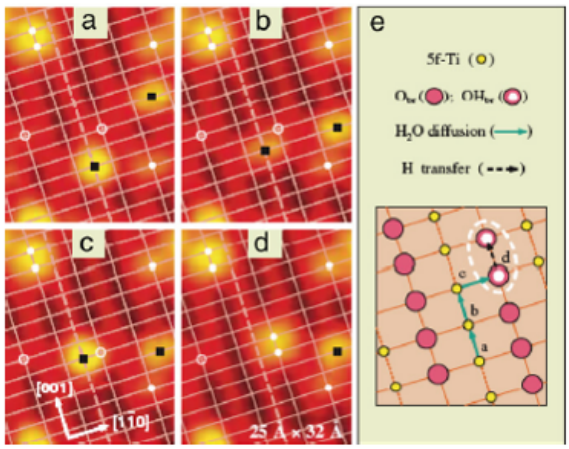


Figure 2.5: STM image demonstrating the proton transfer(taken from Wendt et al [26]).

2.7 Literature review on previous reaction mechanisms

2.7.1 Photo induced organic degradation

The mechanism developed by Zubkov et al [23] suggests that the surface coverage of the contamination decreases when the organic dirt degrades in the presence of sunlight and the decontamination process decreases the contact angle. The studies done by Miyauchi et al [12] on vanadium pentoxide and tungsten oxide demonstrated that these surfaces upon UV illumination exhibits hydrophilicity but cannot degrade organic matter. From this analysis, it is observed that photocatalytic degradation does not decrease the water contact angle. Moreover,this mechanism could not explain the change in contact angle of the clean thin film when exposed to sunlight and water.

The reaction mechanism proposed by Takeuchi et al [22] determined that the formation of a hydrophilic surface is due to heat energy produced by UV illumination. Due to the heating of titanium dioxide, the hydrogen bonds between water and titanium dioxide are disrupted, resulting in the decrease of the surface tension of water on the titanium dioxide surface [22]. This leads to decrease in the contact angle of the water on the titanium dioxide surface. The electrochemical studies done by Sakai et al [15] demonstrated that the photogenerated charges play a vital role in photoinduced hydrophilic reaction mechanism which contradicts the mechanism proposed based upon thermal effects.

2.7.2 Photoinduced oxygen vacancies

In this reaction mechanism holes are trapped in the surface oxygen lattice sites, leading to the release of oxygen molecules from the surface creating oxygen vacancies. The defects created in the surface lattice because of oxygen vacancy increases the affinity for the water [25]. This allows water molecules to be adsorbed at titanium sites and diffuses to oxygen vacancy through titanium sites. In titanium dioxide we have two types of oxygen sites: bridge oxygen sites which are two coordinated and surface and bulk three coordinated oxygen sites. Nakajima et al [14] studied the effect of UV illumination on (110), (100) rutile crystal planes with bridge oxygen atoms, which showed more hydrophilic property than the (001) crystal plane with no bridge oxygen site. These experimental evidences showed that the vacancy sites which are formed at bridge oxygen sites are more reactive than the three coordinated

oxygen sites . Dissociation of water molecule takes place at the vacancy sites when water molecule reach the oxygen vacancies, producing surface hydroxyl groups and releasing protons. The protons jump to neighboring bridge oxygen sites forming bridge hydroxyl groups. In dark conditions, it is observed that the hydrophilic property reverts back to hydrophobic because of the substitution of hydroxyl groups with oxygen molecules from air [4].

The scanning tunneling microscopic studies on $Tio_2(110)$ surface done by Mezhenny et al [13] revealed that under substantial UV illumination oxygen defects are not observed on Tio_2 crystal plane. The conclusions of this research work suggests that the creating of oxygen vacancies mechanism may not produce hydrophilic surfaces.

2.7.3 Photoinduced reconstruction of hydroxyl groups

The photoelectrochemical experimental studies conducted by Sakai et al [15] demonstrated as the potential increases and the concentration of hole scavengers decreases hydrophilicity increases. The conclusion of this study is that photogenerated holes play an important role in the photoinduced hydrophilic reaction mechanism.

In this reaction mechanism the initial hydroxyl groups are produced by oxygen vacancies in vacuum conditions. Upon UV illumination, the photogenerated holes diffuse to the surface of the titanium dioxide and get trapped at oxygen lattice [19]. The trapping of the hole at oxygen lattice site makes the bond between titanium and oxygen weaker and when the water molecules adsorb on the surface it results

in breakage of the bond between titanium and oxygen producing hydroxyl ions. In dark conditions, the hydroxyl group produced from the water desorbs quickly than the lattice oxygen hydroxyl group, which produces the original film before UV irradiation and hydrogen peroxide or water and oxygen. The drawback of this reaction mechanism is to consider the initial hydroxyl groups as produced by oxygen vacancy. As discussed in the earlier section upon UV illumination oxygen vacancies are not formed [13].

Chapter 3: Deposition of titanium dioxide thin films

3.1 Introduction

This chapter gives a brief overview of experiments performed to produce photo-induced hydrophilic films using different precursors. We also discuss about the change in the surface property(hydrophilicity) of the deposited film when exposed to UV illumination and in dark conditions.

3.2 Analysing the photoinduced hydrophilic process

Analytical study of the photoinduced hydrophilic process is done by measuring the contact angle of the water on the titanium dioxide thin film. Surfaces having low contact angle with water are hydrophilic surfaces and those having high contact angle with water are hydrophobic. Sakai et al demonstrated the relationship between the contact angle and the density of the hydroxyl groups [19]. As the surface becomes hydrophilic the contact angle gradually decreases with UV irradiation time. The plot between reciprocal of contact angle and UV irradiation time is a straight line as shown in figure(4.1) and the slope of the plot is defined as the rate of hydrophilic conversion. Based upon these results Sakai et al concluded that these hydroxyl

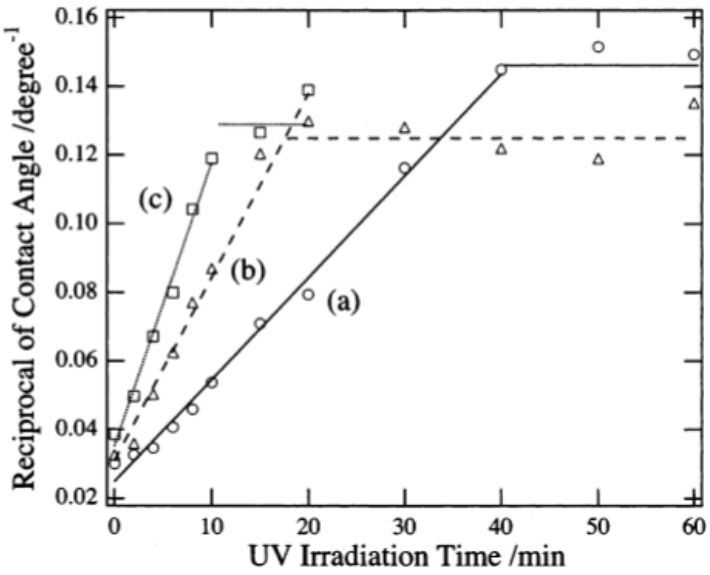


Figure 3.1: Reciprocal of contact angle vs UV irradiation time Graph at differ UV intensities(a) at 0.2m W/cm^2, (b) at 0.7m W/cm^2,(c) 1m W/cm^2 (taken from Sakai et al [19]).

groups are the reconstructed titanium dioxide surface hydroxyl groups [19].

3.3 Experiments

3.3.1 Deposition of titanium dioxide thin film using TDMAT and water as precursors

TDMAT and water precursors are used to deposit titanium dioxide thin film is deposited on the glass substrate at temperature 200^oC in ALD reactor. The reactor pressure is maintained at 10 mbar using pure nitrogen gas as a purge gas. The pulse length for TDMAT was 2 seconds and the purge length was 500 ms. The

pulse length for ozone is 2 seconds and for purge gas is 500ms. The growth rate of this film is 0.55 Å/cycle. The thickness of the film deposited is determined to be around 55 nm using N and K analyzer.The thin film deposited is determined to be amorphous [1].

3.3.2 Deposition of titanium dioxide thin film using TDMAT and ozone as precursors

Photoactive titanium dioxide thin film is deposited on the glass substrate at temperature 225^oC using TDMAT and ozone precursors in ALD reactor. The reactor is operated under 10 mbar pressure using pure nitrogen gas as a purge gas. The pulse length for TDMAT was 2.5 seconds and the purge length was 500 ms. The pulse length for ozone is 2 seconds and for purge gas is 1 second. The total cycle length of the process is six seconds. The growth rate of this film is 0.55 Å/cycle. The studies on the photoactive titanium dioxide films determined that the thickness of the film is in the range of 100 nm-500 nm. The number of cycles required to obtain thickness of 100 nm was determined to be 2000 cycles.The film was deposited for the 2400 cycles. Film thickness is determined by using N and K analyser and the film thickness was measured to be around 110 nm.

3.3.3 Superhydrophilicity

For a photo induced superhydrophilic surface the contact angle of the water on the surface should change upon UV illumination. The change in surface wettability

from hydrophobic to hydrophilic can be determined by measuring the contact angle with respect to UV irradiation time. The film prepared by atomic layer deposition of TDMAT and ozone, and TDMAT and water are tested for photoinduced hydrophilic property. The films used in this experiment are clean films which are solely used to understand photo induced superhydrophilic reaction mechanism.

As discussed in earlier section, for titanium dioxide the maximum wavelength that can be absorbed is 400 nm and this restricted the UV wavelength range. UV light source used in this experiment has the wavelength centered at 365 nm. This can be obtained by using filters and UV lamps. There are three types of UV light: UV-A, UV-B, UV-C. UV-A has wavelength range from 315 nm-400 nm, which is used in our experiment (peak wavelength 365 nm). Blacklight bulb and mercury lamp can be used as UV source as they emit UV-A irradiation. The film is placed under UV illumination of by using 50 W UV mercury bulb.

The change in the contact angle can be measured by using Goniometer or by using a good digital camera and macro lens system. The observations from these experiments after placing the surface under continuous UV illumination for some hours is that the thin film using TDMAT and ozone precursor turns hydrophilic. The experiments conducted on the film deposited using TDMAT and water precursor demonstrated that the contact angle did not change under constant illumination for 24 hours.The reason behind this behavior is change in film characteristics that is crystalline or amorphous nature of the film.

For titanium dioxide film fabricated by using TDMAT and ozone as precursors,it is observed that the contact angle starts changing at t= 3hr and the film

property changes completely into hydrophilic at t=16hr as shown in figure(3.2). As discussed in the earlier section, the studies conducted in dark conditions revealed that the hydrophilic surface reverts back to hydrophobic surface. The titanium dioxide film, which showed hydrophilic property is placed in dark for 2 days and then the surface again turns back to the original condition as shown in the figure(3.2). These experimental studies validated the photo induced superhydrophilicity property of titanium dioxide.

The superhydrophilicity experiments conducted for the titanium dioxide film fabricated by using TDMAT and water as precursors revealed that the contact angle of the water did not changed even after continuous illumination for 24 hours as shown in figure (3.3).The reason behind this behavior is due the surface characteristic of the film. The surface property remained unchanged because of the film deposited is amorphous and amorphous surfaces does not show photoactive property [18].

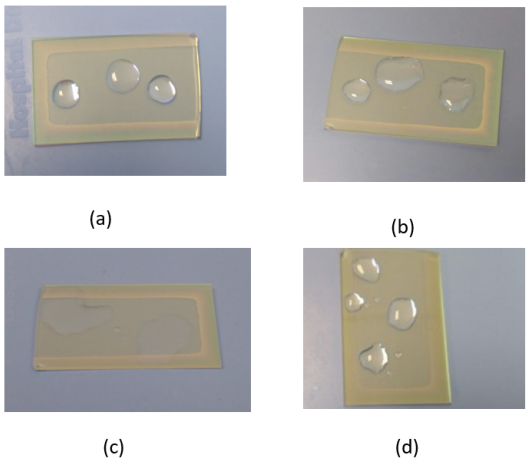


Figure 3.2: The change in the wettability of titanium dioxide film surface deposited by using TDMAT and ozone under UV illumination at different time intervals (a) at t=0, (b) at t=3 hours, (c) at t=16 hours, (d) when placed in dark for two days.

Figure 3.3: The change in the wettability of titanium dioxide film surface deposited by using TDMAT and water under UV illumination (a) at t=0,(b) at t= 24 hours.

Chapter 4: Reaction mechanisms for hydrophilic surfaces

4.1 Overview

In the previous chapter, we have discussed several proposed reactions methods and the inconsistency between them. In this chapter we proposed elementary reaction mechanism for photoinduced hydrophilic surface. The proposed reaction mechanism for photoinduced hydrophilic surface consists of the redox reaction in the presence of sunlight and desorption of hydroxyl groups in dark conditions as show in the figure(4.1).

4.2 Proposed reaction mechanism-(I)

This proposed reaction mechanism is based on the photoinduced oxygen vacancy reaction mechanism, and the elementary reactions in this reaction mechanism are modelled as follows.

The titanium dioxide film is exposed to sunlight or UV illumination, which results in generation of holes and electrons .

$$hv \longrightarrow h^{+} + e^{-}$$

These photogenerated holes and electrons recombine in the bulk and produced heat

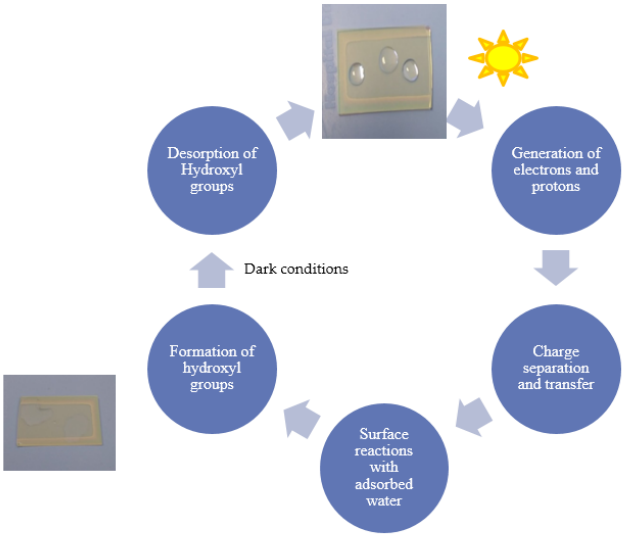


Figure 4.1: Overview of reaction mechanisms.

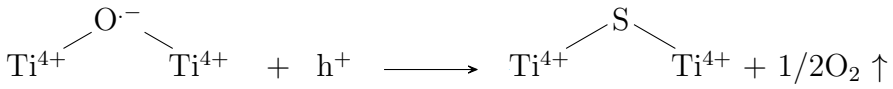
energy which is called as bulk recombination.The holes and electrons diffuses to surface and gets recombine at the surface which is called as surface recombination.

$$h^+ \quad + \quad e^- \quad \longrightarrow \quad \text{hv or heat}$$

The photogenerated holes, which avoided recombination diffuse to the surface and get trapped in the oxygen lattice [25].

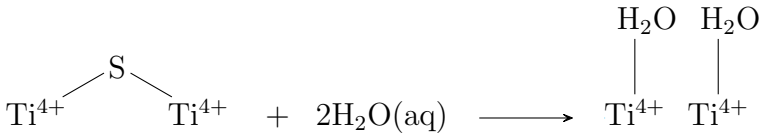
$$Ti^{4+}\!-\!O^{2-}\!-\!Ti^{4+} \quad + \quad h^+ \quad \longrightarrow \quad Ti^{4+}\!-\!O^{\cdot -}\!-\!Ti^{4+}$$

The oxygen vacancy is created when more number of holes get trapped in the oxygen lattice. The oxygen is released from the surface in the form of a molecule due to which the reaction happens with adjacent bridge hydroxyl groups forming two oxygen vacancy sites (S) [25].

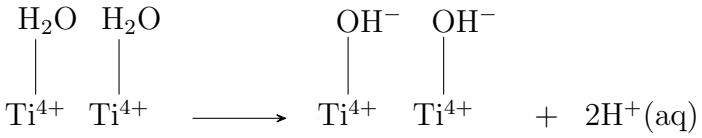


When water molecules are adsorbed on titanium sites, dissociative adsorption of water takes place. The interaction of water molecule is studied in the following reactions.

Adsorption of water at titanium sites

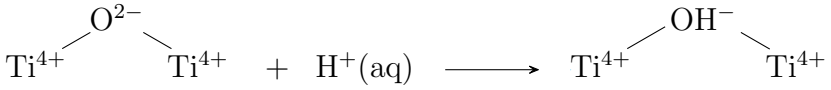


Formation of surface hydroxyl groups and release of proton



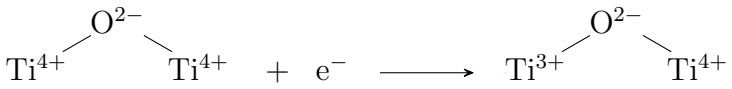
The released proton can be transferred to neighboring bridge oxygen sites or react with superoxide radical anion, which is produced by reduction of molecular oxygen to form hydroperoxyl radical $HO_2^{\cdot}$.

Pathway 1- Transfer of protons to neighboring bridge oxygen sites.

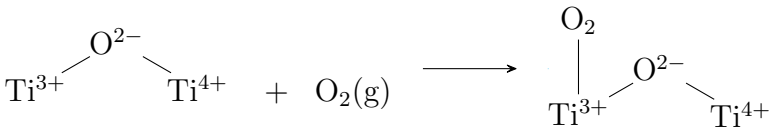


Pathway 2- Formation of $HO_2^{\cdot}$ radical.

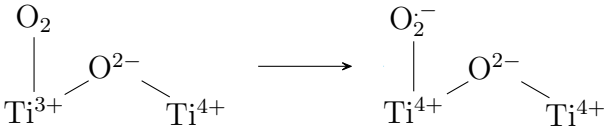
The photogenerated electrons react with adsorbed molecular oxygen on titanium sites to form superoxide anion radical [6]. This superoxide anion is an active oxygen species which further decomposes organic matter. The reduction of molecular oxygen is modelled as follows. The photogenerated electrons which avoided recombination and reached the surface are trapped at titanium sites.



The experiment analysis from literature review demonstrated that when the surface is exposed to molecular oxygen, adsorption of molecular oxygen take place [6].



The adsorbed molecular oxygen takes the electron from Ti^{3+} forming superoxide radical anion [21].



In dark conditions the property of the film changes from hydrophilic to hydrophobic and the original characteristic of the film is recovered. Presence of oxygen in

dark conditions results in oxygen adsorption and dissociation to recover the surface structure before UV illumination [4].

This reaction mechanism is not a viable mechanism because the experiment studies conducted by Mezhenny et al [13] revealed that the oxygen vacancies are not created under substantial UV illumination. The important reaction step in this reaction mechanism is creation of oxygen vacancies by photogenerated holes.From this analysis we can say that the photoinduced superhydrophilicity is not due to creation of surface vacancies.

4.3 Proposed reaction mechanism-(II)

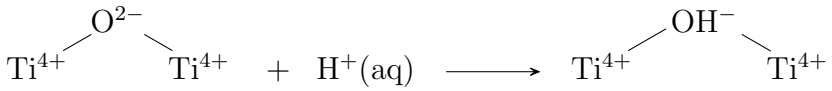
This reaction mechanism based on principles explained photoinduced reconstruction of hydroxyl ions. In this reaction mechanism the bond between oxygen and titanium gets weaker due to the trapping holes at oxygen lattice. This reaction mechanism is modelled as follows.

When the surface is exposed to sunlight and photons energy is greater than the band gap energy of titanium dioxide holes and electrons are generated.

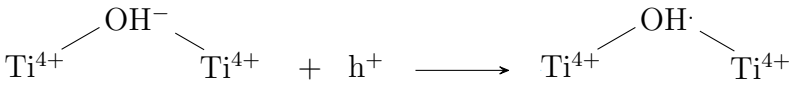
$$hv \longleftrightarrow h^{+} + e^{-}$$

The initial hydroxyl group in this mechanism is formed by creating oxygen vacancy in vacuum condition [19]. The formation hydroxyl groups is not a viable mechanism because the oxygen vacancies are not generated by holes. Based on the electrochemical study conducted on titanium dioxide a modified mechanism is proposed [6]. The proton is available from the water because the water is acidic in nature. From the

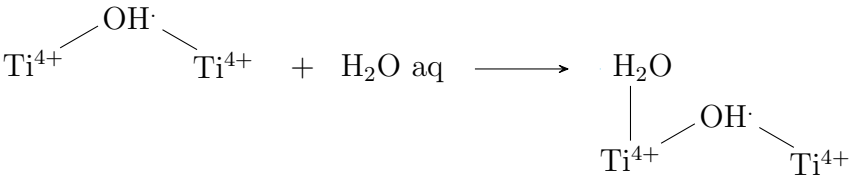
study on ph analysis of the water, it is observed that the formation of hydroxyl ions is favorable at low values of ph [5]. Moreover, the ph of rain is 5.8 which supports the presence of proton.



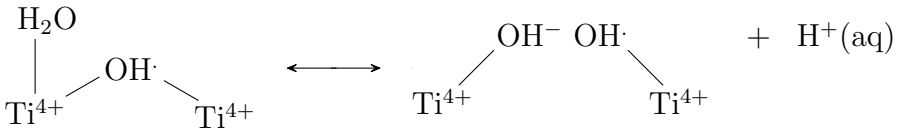
The photogenerated holes are trapped in oxygen lattice site forming hydroxyl radical.The trapping of hole at oxygen lattices makes the bond between titanium and oxygen weaker.



Adsorption of water on the titanium sites.



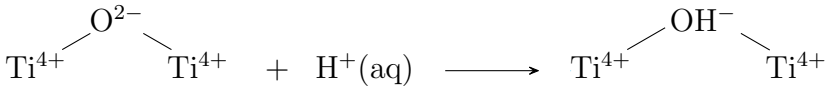
The bond between oxygen and titanium breaks and hydroxyl groups are formed when water gets adsorbed on the surface of titanium dioxide.



The released proton can be transferred to neighboring bridge oxygen sites or react with superoxide radical anion, which is produced by reduction of molecular oxygen

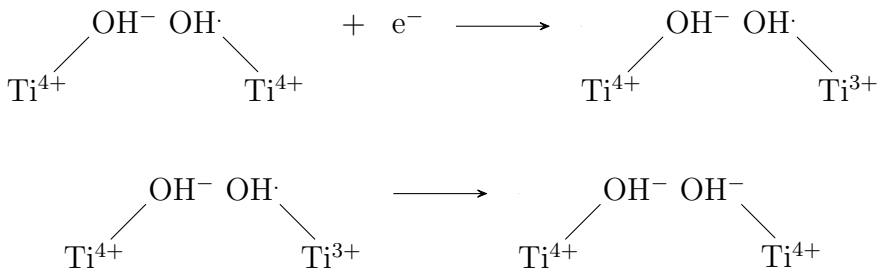
to form hydroperoxyl radical or $HO_2^{\cdot}$ [6].

Pathway 1- Transfer of protons to neighboring bridge oxygen sites.



Pathway 2- Formation of $HO_2^{\cdot}$ radical.

From the literature review, it is observed that most of the photogenerated electrons are free electrons in $Ti^{+}3$ form . This electron is transferred to hydroxyl radical forming hydroxyl ion. [21] .



From the experimental studies it is observed that the desorption energy of the hydroxyl ion formed by water molecule is very low [19]. In dark conditions, due to low desorption energy of hydroxyl group formed by water molecule, the hydroxyl group desorbs from the surface in the form of the water molecule.

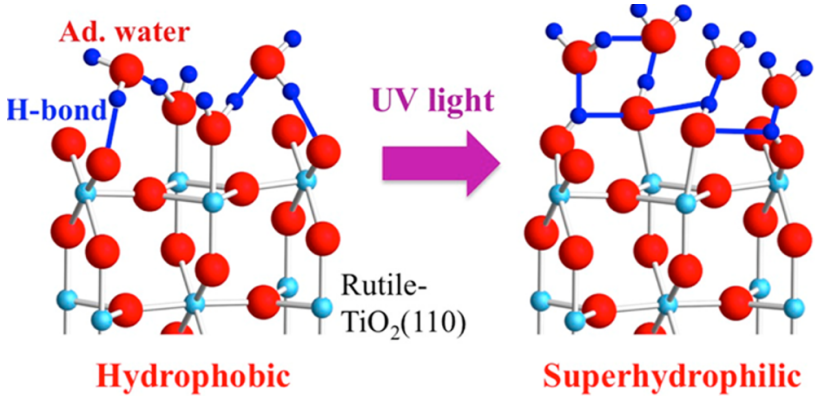
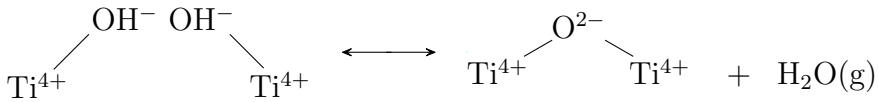


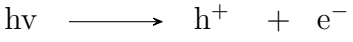
Figure 4.2: Structural model for photoinduced superhydrophilicity (taken from Shirasawa et al. [20]).



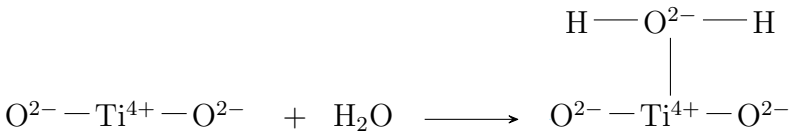
4.4 Proposed reaction mechanism -(III)

In this reaction mechanism the surface hydroxyl groups are formed without any creation of defect or breaking the bonds between titanium and oxygen as shown in the figure(4.2). The hydroxyl groups are formed due to the electron-proton transfer reactions [6]. Elementary reaction mechanism is modeled as follows.

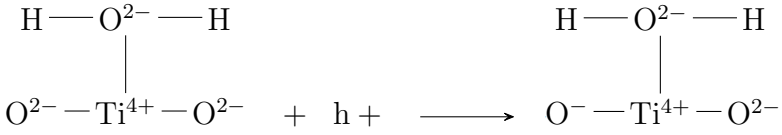
Generation of electrons and holes when exposed to sunlight



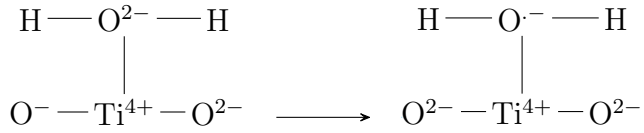
Adsorption of water molecules at titanium site



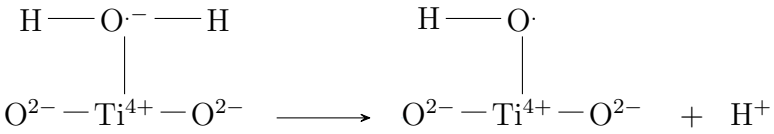
The photogenerated holes are trapped in oxygen lattice.



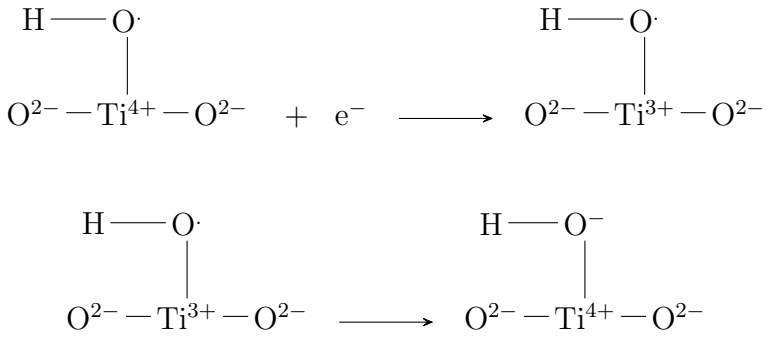
The electrons from oxygen in water molecule are transferred to oxygen lattice site with holes trapped [6].



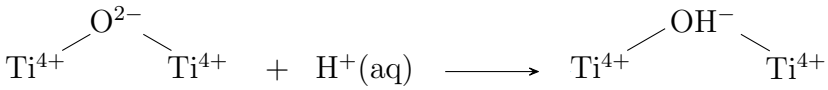
The transfer of electrons from the oxygen of adsorbed water results in the release of protons from water molecule forming hydroxyl groups on the surface of titanium dioxide.



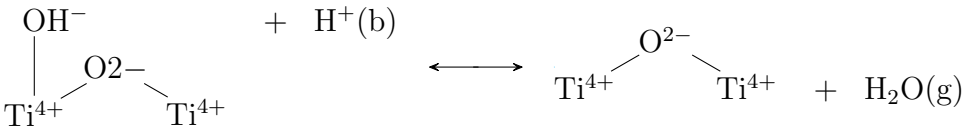
The electron is found in the form of $Ti^{+}3$ ion. This electron is transferred to hydroxyl radical forming hydroxyl ion.



The proton is released from the water while forming hydroxyl groups on the surface of titanium dioxide.The proton can be transferred to neighboring bridge sites [20].



The desorption energy of hydroxyl groups formed by water molecule are low in dark conditions. The hydroxyl groups get desorbed form the surface due to low desorption energy forming water vapor [19]. The hydroxyl group takes hydrogen from the bridge hydroxyl groups forming water vapor.



Chapter 5: Conclusions and future work

An objective of this thesis is to develop a self consistency reaction mechanism for photoinduced hydrophilicity. The previously proposed reaction mechanisms have some drawbacks, which made understanding the elementary photoinduced hydrophilic reaction mechanism challenging. Based on the experiment analysis obtained from literature review the main reaction steps in photoinduced superhydrophilic phenomena are generation of electrons and holes when exposed to sunlight, trapping of holes, adsorption of water on titanium sites, reaction between holes and water molecules to produce hydroxyl groups, release of protons, molecular oxygen adsorption at titanium sites, formation of superoxide anions and dehydroxylation in dark conditions. Elementary oxidation and reduction reactions of photoinduced superhydrophilicity are proposed and they support the experiment evidence. From the experimental studies of UV illumination on titanium dioxide surface, it is observed that the proposed reaction mechanism based on the creation of oxygen vacancies is not a viable reaction mechanism. The potential reaction mechanisms are reaction mechanisms based on the reconstruction of hydroxyl groups and electron transfer reactions.

Undoped titanium dioxide films were deposited using TDMAT and ozone, and

TDMAT and water precursors in ALD reactor. The films are deposited at high temperatures to obtain a crystalline titanium dioxide film. These thin films are placed under UV illumination for several hours to test the photoinduced superhydrophilic property. The observations from this experiment are that the initial contact angle of the film is high and after exposing the film to UV illumination for some hours the film contact angle changes to almost 0^O. After placing in dark condition for two days, the contact angle becomes higher which are promising results.

The films deposited by using TDMAT and ozone precursor turned hydrophilic upon constant UV illumination but the films deposited by using TDMAT and water did not turn hydrophilic. The difference in behaviour of these two films is due to the surface characteristics:the film deposited by TDMAT and water is amorphous and by TDMAT and ozone is crystalline. From the literature review it is observed that the amorphous films are not photoactive and crystalline films are photoactive as they turn hydrophilic upon UV illumination.

The analysis proposed reaction mechanism can extend to reaction network analysis. In our research groups we use reaction network tools to say whether the reaction is proper or not. By utilizing this technique we can further support the proposed reaction mechanism.

The factors effecting the photoinduced superhydrophilicity such as UV illumination, thickness, film characteristic can further be studied.The rate of the hydrophilicity depends on the intensity of UV illumination. By changing the UV illumination we can observe the changes in the surface property of the film. Additional experimental analysis such as X-ray Powder Diffraction (XRD) are required to iden-

tify whether the film is crystalline or amorphous. The analysis from the XRD studies will further support the superhydrophilicity experiments. Experiment analysis by changing the ph of water can be used to determine the effect of protons concentration in photoinduced superhydrophilicity mechanism. This will further support the study on potential reaction mechanism for photoinduced superhydrophilicity.

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